Size effects in the structure factor of a system with partial translational ordering

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The static structure factor for liquid crystals formed by disk-like molecules is calculated. It is shown that size effects occur in a two-dimensional lattice of liquid columns consisting of such molecules if the samples are much larger than the corresponding anisotropic three-dimensional crystals.

1. INTRODUCTION

It is known[1] that the most important parameter of a condensed system is the static structure factor $S(q)$, which determines the integral characteristics of the scattering, say of neutrons or x rays. In ordinary three-dimensional crystals $S(q)$ consists of an aggregate of Bragg peaks (whose position is determined by reciprocal-lattice vectors) and a certain diffuse background. This separation of the scattered radiation into regular reflections and a diffuse background is possible, strictly speaking, only in infinite crystals. In this case, the terms proportional to δ functions in the expressions for the scattering intensity describe the regular reflections, while the terms that do not contain δ functions describe the smooth distribution of the diffuse scattering. The thermal oscillations in three-dimensional systems lead to a weakening of the intensity of the regular reflection on account of the Debye-Waller factor but do not cause line broadening. In crystals with finite dimensions ($\sim R$), the δ functions are replaced by certain peaks of finite width $\sim 1/R$, and in this sense are indistinguishable from the diffuse background. Actually, however, the characteristic widths of the diffuse background, for wave vectors in the vicinity of the Bragg maxima, greatly exceed the δ-peak width connected with the sample dimensions. Indeed, in an isotropic three-dimensional system the characteristic inhomogeneity of the diffuse background is of the order of $E/\tau^2 T$ (where E is the elastic modulus, τ is the reciprocal-lattice constant, and T is the temperature). At typical values of the parameters ($E \sim 10^{11}$ erg/cm^3, $\tau \sim 10^8$ cm^{-1}, $T \sim 10^{-14}$ erg) this quantity is $\sim 10^9$ cm^{-1}, much larger than the width $1/R$ of the Bragg peaks at all the permissible sample dimensions.

The situation is different in systems with partial translational ordering, represented by the great variety of types of liquid crystals. For example, if we are dealing with one-dimensional translational order (smectic liquid crystals), there are no δ-function Bragg peaks at all in an infinite sample, since the Debye-Waller factor diverges. In the vicinity of the reciprocal-lattice sites, however, the structure factor is singular, as reflected by the slow (logarithmic) decrease of the order in such systems. The structure factor of such systems was calculated by Feigelman and Pokrovsky[2] as well as by Gunther *et al.*[3] Competing for a finite system with a smectic order are the anomalous part of the diffuse background and quasi-Bragg scattering (since the Debye-Waller factor does not diverge in a system with finite dimensions). Depending on the parameters of the system, a finite sample of a smectic liquid crystal behaves, in the sense of scattering of x rays and neutrons, either like an ordinary crystal (i.e., it has relatively narrow Bragg peaks), or like an infinite smectic (i.e., the singular diffuse background predominates). As already mentioned, the structure factor of systems with smectic order has already been investigated earlier.[2,4]

A few years ago, Chandrasekhar[5] discovered new types of liquid crystals, called diskotics, with two-dimensional translational order. There are very few papers on this topic, (see, e.g., the review[6]) owing to the difficulty of producing and ordering these mesophases. Definite progress has been made in this direction by now, however.[7] The principal method of determining the structures of these mesophases is to study the scattering of x rays. It is most convenient here to use a geometry in which the scattering is in the plane of a two-dimensional lattice of a diskotic phase. The most important question from the experimental point of view is how to distinguish the Bragg peaks of a two-dimensional lattice made up of liquid columns of the diskotic phase from the corresponding Bragg peaks of an ordinary three-dimensional crystal structure. This question will be answered in Sec. 3 below.

2. DISKOTIC LIQUID CRYSTALS

We consider first the general characteristics of mesophases produced by a lattice of liquid columns. The order parameter is in this case a set of complex amplitudes $\psi(q)$ that define a two-dimensional lattice, and the director vector n, which specifies the average orientation of the planes of the disk-like molecules.[8,9] In the simplest case n is perpendicular to the plane of the two-dimensional lattice (and is a tangent vector to the liquid columns that make up this lattice). The system is in this case obviously invariant to simultaneous rotation of n and of the plane of the two-dimensional lattice. Taking this circumstance into account, we have the following Landau expansion of the free energy of the diskotic in powers of $\psi(q)$

$$\delta F = \frac{1}{2}a\sum_{q}\psi(\mathbf{q})\psi(-\mathbf{q}) - \frac{1}{3}b\sum_{q_1,q_2,q_3}\psi(\mathbf{q}_1)\psi(\mathbf{q}_2)\psi(\mathbf{q}_3)\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)$$

$$+\frac{1}{4}c\sum_{q_1,q_2,q_3,q_4}\psi(\mathbf{q}_1)\psi(\mathbf{q}_2)\psi(\mathbf{q}_3)\psi(\mathbf{q}_4)\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3+\mathbf{q}_4)$$

$$+D_{\parallel}\sum_{q}\left|\left(\frac{d}{dz}+iq\delta n\right)\psi(\mathbf{q})\right|^2 + D_{\perp}\sum_{q}|\nabla_{\perp}\psi(\mathbf{q})|^2 + \frac{1}{2}K_{33}[\mathbf{n}_0\times\text{rot}\,\delta\mathbf{n}]^2. \tag{1}$$

Here, a, b, c, $D_{\parallel}$, and $D_{\perp}$ are the expansion coefficients, K_{33} is the longitudinal bending modulus of the n field. In the diskotic phase, the rigid two-dimensional lattice admits of only such a deformation, but when the two-dimensional lattice melts and the nematic phase is formed, other deformations are also possible (transverse bending and twist, described by the corresponding Frank moduli K_{11} and K_{22}).

Let us explain also the origin of the gradient terms. As already mentioned, $\psi(\mathbf{q})$ describes the two-dimensional modulation of the density ρ_1 in the lattice of liquid columns:

$$\rho_1(x,y) = \sum_{q}\psi(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}}$$

[$\mathbf{r}$ denotes the radius vector in the (x, y) plane, and the three-dimensional radius vector is $\mathbf{R} = (\mathbf{r}, z)$]. It must be recognized here that the amplitudes $\psi(\mathbf{q})$ are generally speaking slow functions of R, i.e., $\nabla\psi(\mathbf{q}) \ll q\psi(\mathbf{q})$. The gradient terms in (1) stem from expressions of the type $[(\mathbf{n}\nabla)\rho_1]^2$ and $([\mathbf{n}\times\nabla]\rho_1)^2$ with account taken of the inequality written out above. Of course, such a simple form (the presence of only one coefficient $D_{\perp}$) is a first rough approximation, since the elastic deformations of even an isotropic (for example, hexagonal) lattice are described by two moduli.

One more circumstance is that the expansion (1) corresponds to the straight diskotic phase D_0. In principle, an even less symmetrical structure is possible, in which the tangents to the liquid columns do not coincide with the normals to the plane of the two-dimensional lattice. In such an oblique diskotic structure D_t, the free energy differs from (1) only in the form of the gradient terms. It is convenient to introduce the vector $\boldsymbol{\beta}$, which describes the deviation of the director n from the tangent ν to the liquid column. Then the gradient terms in (1) take the form

$$D_{\parallel}\sum_{q}\left|\left\{\frac{d}{dz}+i(q\delta n+\beta q)\right\}\psi(\mathbf{q})\right|^2 + D_{\perp}\sum_{q}|\nabla_{\perp}\psi(\mathbf{q})|^2$$

(we have assumed that the angle between n and ν is small, i.e., $|\boldsymbol{\beta}| \ll 1$). In the general case we have also a certain expansion of the free energy in powers of $\boldsymbol{\beta}$ and $\nabla\boldsymbol{\beta}$. We thus obtain the complete phase diagram of the D_0, D_t, and N_D phases (N_D is the nematic phase made up of disk-like molecules). This diagram has a triple point at which the stability regions of all three phases are in contact. The transitions $D_0 \leftrightarrow N_D$ and $D_t \leftrightarrow N_D$ are of first order, while $D_0 \leftrightarrow D_t$ can in principle be a second-order phase transition.

The foregoing analysis corresponded to an experimental situation in which the liquid columns also vanish when the two-dimensional lattice is melted, and we obtain the N_D phase. If the liquid columns were to be preserved in such a melting, we would obtain a phase similar to a polymer nematic.[1] This question, however, is outside the scope of the present paper. Being interested only in the structure factor of the D_0 phase, we shall investigate expression (1) for the free energy.

It is convenient to introduce the modulus and the phase of the order parameter:

$$\psi(\mathbf{q}) = m(\mathbf{q})e^{i\varphi(\mathbf{q})}. \tag{2}$$

Substituting (2) in (1) we obtain

$$\delta F = \frac{1}{2}a\sum_{q}m(\mathbf{q})m(-\mathbf{q}) - \frac{1}{3}b\sum_{q_1,q_2,q_3}m(\mathbf{q}_1)m(\mathbf{q}_2)m(\mathbf{q}_3)\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)$$

$$+\frac{1}{4}c\sum_{q_1,q_2,q_3,q_4}m(\mathbf{q}_1)m(\mathbf{q}_2)m(\mathbf{q}_3)m(\mathbf{q}_4)\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3+\mathbf{q}_4)$$

$$+D_{\parallel}\sum_{q}\left[\frac{dm(\mathbf{q})}{dz}\right]^2 + D_{\perp}\sum_{q}[\nabla_{\perp}m(\mathbf{q})]^2 + D_{\parallel}\sum_{q}m^2(\mathbf{q})\left[\frac{\partial\varphi}{\partial z}+q\delta n\right]^2$$

$$+D_{\perp}\sum_{q}m^2(\mathbf{q})[\nabla_{\perp}\varphi(\mathbf{q})]^2 + \frac{1}{2}K_{33}[\mathbf{n}_0\,\text{rot}\,\delta\mathbf{n}]^2. \tag{3}$$

Minimization of δF with respect to the modulus $m(\mathbf{q})$ yields the following results. At a temperature $T_c = T^* + 2b^2/9\alpha c$ ($a = \alpha(T - T^*)$) we have a first-order phase transition from the N_D phase (in which $m = 0$) into the D_0 phase, in which the distribution of m in the ground state is uniform in space:

$$m = \frac{b}{2c}\left\{1 + \left[1 - \frac{4ac}{b^2}\right]^{1/2}\right\}.$$

We consider for the sake of argument only a hexagonal lattice of liquid columns and take into account the principal period $\mathbf{q}_0$ ($m(\mathbf{q}_0) \equiv m_0$):

$$\delta F = D_{\parallel}m_0^2\sum_{q}\left[\frac{\partial\varphi}{\partial z}+q_0\delta n\right]^2$$

$$+D_{\perp}m_0^2\sum_{q}(\nabla_{\perp}\varphi)^2 + \frac{1}{2}K_{33}[\mathbf{n}_0\,\text{rot}\,\delta\mathbf{n}]^2. \tag{4}$$

To exclude the fluctuations of the director it is necessary also to minimize (4) with respect to $\delta\mathbf{n}$. We obtain thus an expression that depends only on the spatial derivatives of the phase:

$$\delta F = D_{\perp}m_0^2(\nabla_{\perp}\varphi)^2 + \frac{1}{2}\frac{K_{33}}{q_0^2}\left(\frac{\partial^2\varphi}{\partial z^2}\right)^2. \tag{5}$$

Equation (5) agrees with the known theorem of Landau and Peierls,[10] that in such a two-dimensional lattice of liquid columns the correlation function of the displacements takes the form:

$$\langle u, u\rangle \sim [q_z^4 + \text{const}\,q_{\perp}^2]^{-1}. \tag{6}$$

Indeed, by minimizing (4) with respect to $\delta\mathbf{n}$ we obtain

$$d\varphi/dz + q_0\delta n = 0.$$

From the definition of the phase of the order parameter and from the obvious connection between the displacements of the two-dimensional lattice with the deviations of the liquid columns (with the director fluctuations in the case of the D_0 phase) we have $\varphi = \mathbf{q}_0\cdot\mathbf{u}$.

Thus, Eq. (5) is an approximate expression for the elastic energy of the D_0 phase. It is easy to write also the total form of the elastic energy. For example, for a hexagonal lattice of liquid columns we have the following generalization of Eq. (5):

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$$\delta F = \frac{1}{2} C_{11}\left[\left(\frac{\partial u_x}{\partial x}\right)^2 + \left(\frac{\partial u_y}{\partial y}\right)^2\right] + C_{12}\frac{\partial u_x}{\partial x}\frac{\partial u_y}{\partial y}$$

$$+ \frac{1}{4}(C_{11}-C_{12})\left(\frac{\partial u_x}{\partial y}+\frac{\partial u_y}{\partial x}\right)^2 + \frac{1}{2}C_{33}\left(\frac{\partial u_z}{\partial z}\right)^2 + C_{13}\frac{\partial u_z}{\partial z}\left(\frac{\partial u_x}{\partial x}+\frac{\partial u_y}{\partial y}\right)$$

$$+ \frac{1}{2}K_{33}\left[\left(\frac{\partial^2 u_x}{\partial z^2}\right)^2 + \left(\frac{\partial^2 u_y}{\partial z^2}\right)^2\right]. \tag{7}$$

We used in (7) the standard notation for the elastic moduli and [in contrast to (5)] took into account the possible compression deformation of the liquid columns $\partial u_z/\partial z$. Equation (7) differs also from the expression for the elastic energy of the three-dimensional crystal with hexagonal symmetry. The point is that in the D_0 phase the relative shift of the liquid columns does not lead to an elastic energy $\sim q^2$. The corresponding shear modulus is therefore zero.

We introduce for convenience somewhat different symbols. The displacements in the two-dimensional lattice will be designated by u_α ($\alpha = 1,2$), and the displacement along the liquid columns by v. Similarly, q_α are the wave vectors of the two-dimensional deformation and $\varkappa$ is the component of the wave vector along the z axis. In this notation, the expression for the elastic energy (7) can be written as follows:

$$\delta F = \frac{1}{2}\int\frac{d\varkappa\, d^2q}{(2\pi)^3}\{(C_{11}+C_{12})|q_\alpha u_\alpha|^2 + (C_{11}-C_{12})q^2|u_\alpha|^2 + C_{33}\varkappa^2|v|^2$$

$$+ K\varkappa^4|u_\alpha|^2 + C_{13}q_\alpha\varkappa u_\alpha v^*\}. \tag{8}$$

Similarly, in the single-constant approximation (5) we have

$$\delta F = \frac{1}{2}\int\frac{d\varkappa\, d^2q}{(2\pi)^3}\{[Cq^2+K\varkappa^4]u_\alpha^2 + E\varkappa^2 v^2\}, \tag{9}$$

where $C = D_\perp m_0^2 q_0^2$, $E \sim C_{33}$. From (9) we obtain the following expression for the correlators:

$$\langle u_\alpha u_\beta\rangle = \frac{T\delta_{\alpha\beta}}{Cq^2+K\varkappa^4}, \quad \langle u_\alpha v\rangle = 0, \quad \langle v^2\rangle = \frac{T}{E\varkappa^2}, \tag{10}$$

or more accurate formulas that follow from (8)

$$\langle u_\alpha u_\beta\rangle = T\left\{\frac{\delta_{\alpha\beta}-e_\alpha e_\beta}{(C_{11}-C_{12})q^2+K\varkappa^4} + \frac{e_\alpha e_\beta}{C_{11}q^2+K\varkappa^4}\right\},$$

$$\langle v^2\rangle = \frac{T}{C_{33}\varkappa^2}, \quad \langle u_\alpha v\rangle = \frac{Tq_\alpha\varkappa C_{13}}{[C_{11}q^2+K\varkappa^4]C_{33}\varkappa^2}. \tag{11}$$

where e is the unit vector that defines q. We see that qualitatively (11) and (10) lead to the same dependences on q and $\varkappa$, differing only in the tensor structure and in the values of the elastic moduli.

3. THE STRUCTURE FACTOR

From the definition of the structure factor S we have

$$S(\mathbf{q},\varkappa) = \left|\sum_\mathbf{a} e^{i\mathbf{q}\mathbf{a}}\right|^2\langle e^{iq_\mathbf{a}u+i\varkappa v}\rangle + \sum_{\mathbf{a},\mathbf{a}'}e^{i\mathbf{q}(\mathbf{a}-\mathbf{a}')}\langle\exp\{iq(\mathbf{u}_\mathbf{a}-\mathbf{u}_{\mathbf{a}'})+i\varkappa(v-v')\}\rangle \tag{12}$$

(a is the vector of the two-dimensional lattice of the liquid columns). The first term in (12) corresponds to coherent Bragg scattering, and the second describes the diffuse background (incoherent scattering). We start with coherent scattering:

$$S_c(\mathbf{q},\varkappa) = \left|\sum_\mathbf{a} e^{i\mathbf{q}\mathbf{a}}\right|^2\langle e^{iq_\mathbf{a}u+i\varkappa v}\rangle. \tag{13}$$

In the usual manner, the first sum in an infinite crystal yields δ-function Bragg maxima, and the second multiplier yields the Debye-Waller factor

$$\left|\sum_\mathbf{a}\exp(i\mathbf{q}\mathbf{a})\right|^2 = N\frac{(2\pi)^2}{v_0}\sum_\tau\delta(\mathbf{q}-\tau), \tag{14}$$

$$\langle e^{iq_\mathbf{a}u+i\varkappa v}\rangle \equiv e^{-2W}.$$

Here v_0 is the area of the unit cell of the two-dimensional lattice, N is the number of cells, and τ is the reciprocal-lattice vector. In a finite crystal, the δ functions are replaced by certain (dependent on the sample shape) δ-like functions with width $1/R$.

Less trivial size effects can manifest themselves in the Debye-Waller factor. In the harmonic approximation

$$2W = \langle[q_\alpha u_\alpha + \varkappa v]^2\rangle. \tag{15}$$

Substituting here expressions (10) for the correlators, we obtain

$$2W = \frac{q^2}{(2\pi)^3}\int d^2p\, dt\left[\frac{T}{Cp^2+Kt^4}\right] + \frac{\varkappa^2}{(2\pi)^3}\int d^2p\, dt\frac{T}{Et^2}. \tag{16}$$

In principle, size effects of different types are possible. In the simplest case it can be assumed that the properties of a finite system are the same as those of an infinite one. In other words, we can consider an infinite system, but the scattering is effected in some small part of this system. All the size effects are simply connected in this case with the restrictions on the integration region in (16). We consider a system with dimensions $L'\times L'\times L$ (L is in the direction of the liquid columns).

The problem has a characteristic parameter with dimension of length

$$\Lambda = (K/C)^{1/2}. \tag{17}$$

Far from the transition into the nematic phase, Λ is of the order of the molecular dimension d, but in the vicinity of the transition point we have $C \to 0$ and $\Lambda \to \infty$. The second term in (16), which holds at $\varkappa \neq 0$, describes scattering by the liquid columns. The dimensional dependences of the corresponding contribution to the Debye-Waller factor are trivial:

$$2W_l = \frac{\pi T\varkappa^2}{Ea^2}L\left(1-\frac{a^2}{L'^2}\right)$$

(a is the lattice period of the liquid columns).

We note, however, that the "liquid" contribution $2W_l$ is practically independent of the dimension L'.

We consider now the case $\varkappa = 0$. The scattering is determined by the liquid-column lattice. Let $L' \to \infty$ (what is actually required is $\Lambda L' \gg L^2$). We then have

$$2W_l = \frac{Tq^2}{(2\pi)^2CL}\int\frac{d^2p}{p^2} + \frac{Tq^2}{C(2\pi)^3}\int\frac{d^2p\, dt}{p^2+\Lambda^2 t^4}. \tag{18}$$

The first term in (18) describes the contribution of one lattice layer, the second the contribution from the three-dimensional system. We thus get from (18)

$$2W_l = \frac{Tq^2}{2\pi CL}\ln\frac{L'}{d} + \frac{Tq^2}{2\pi^2 C(\Lambda q)^{1/2}}\left[\varphi\left(\frac{(a\Lambda)^{1/2}}{d}\right)-\varphi\left(\frac{(a\Lambda)^{1/2}}{L}\right)\right], \tag{19}$$

where

$$\varphi(u) = \int_0^u dx\ln(1+1/x^4),$$

$$\varphi(u) = -4u\ln u + u\ln(1+u^4) + \frac{1}{2^{1/2}}\ln\frac{1+2^{1/2}u+u^2}{1-2^{1/2}u+u^2} + \frac{1}{2^{1/2}}\operatorname{arctg}\frac{2^{1/2}u}{1-u^2}.$$

The asymptotic forms of this functions are

$$\varphi(u) \approx -4u \ln u \quad \text{as} \quad u \to 0,$$
$$\varphi(u) \approx 2^{-7/2}\pi \quad \text{as} \quad u \to \infty.$$

To be able to observe size effects in this case we must satisfy the following inequality:

$$L \lesssim \frac{\pi(\Lambda a)^{1/2}\ln(L'/d)}{\varphi((\Lambda a)^{1/2}/d)} \equiv L_{c2}. \tag{20}$$

This condition is similar to that obtained in Ref. 2 for anisotropic three-dimensional crystals. A subdivision such as (18) of the Debye-Waller factor into two-dimensional and three-dimensional contributions has the following meaning. In fact, we have in place of (18) a sum over the whole-number vectors $t = 2\pi n/L$. Equation (18) corresponds to separation of the term $n = 0$ and replacement of all the remaining terms of the sum by an integral with respect to t. This replacement is justified because in our system there is a mode with $t = 0$, in which the crystal layers are shifted as a whole. Such a mode is permissible only if the diskotic liquid crystal layer has free boundaries. On the other hand, since the dependences on n are slow enough (logarithmic), we can confine ourselves with good accuracy to separation of only the term with $n = 0$. As $L^2 \sim L'\Lambda \to \infty$ the two-dimensional contribution to the Debye-Waller factor tends to zero and a transition takes place thus to the "volume" case.

The situation is different at $L^2 \gg L'\Lambda$. In this case we must replace by a sum in (16) or (18) also the integral over the transverse momenta:

$$2W_t = \frac{2\pi Tq^2}{CL'^2} \sum_{m,n} \int \frac{dt}{\Lambda^2 t^4 + (m^2+n^2)4\pi^2/L'^2}. \tag{21}$$

Separation of the term with $m = n = 0$ in (21), however, is inadmissible. The point is that such a mode would correspond to a synchronous flexure of all the liquid chains, and consequently to simply a flexure of the entire sample as a whole. By itself, a cylindrical sample of a diskotic liquid crystal is not stable to such a flexure. Flexure of the entire sample as a whole is forbidden by the boundary conditions (simply speaking, by the presence of rigid walls of the vessel containing the liquid crystal).

The integral in (21) converges and can be easily calculated

$$2W_t = \frac{Tq^2\pi^{1/2}}{8C} \frac{1}{(\Lambda L')^{1/2}} \sum_{m,n} \frac{1}{(m^2+n^2)^{1/2}}. \tag{22}$$

To determine this double sum it is convenient to use the known Euler-Maclaurin theorem:

$$\sum_a^b f(x) = \frac{1}{h}\int_a^b f(x)\,dx - \frac{1}{2}[f(b)-f(a)] - \frac{B_1}{2!}h[f'(b)-f'(a)] + \dots$$
$$\dots + (-1)^{k-1}\frac{B_k}{(2k)!}h^{2k-1}[f^{(2k-1)}(b)-f^{(2k-1)}(a)] + \dots,$$

where B_k are Bernoulli numbers and $f^{(k)}$ is the kth derivative of the function $f(x)$.

In this case, this formula should be used twice. We consider first the function $f = (x^2 + n^2)^{-3/4}$. The summation interval is $h = 1$. It is the difference between the sum and the corresponding interval which is the size effect of interest to us. The most substantial contribution to this difference is due to small values of m and n. In

the principal approximation in $1/L'$ we replace $\sum_m$ simply by an integral, and in the second summation, now already with the function $f(z) = z^{-1/2}$, we take into account the first two terms in the Euler-Maclaurin formula. We thus obtain

$$2W_t = \frac{Tq^2\pi^{1/2}}{8C(\Lambda a)^{1/2}}\left\{1 - \left(\frac{a}{L'}\right)^{1/2}\right\}. \tag{23}$$

We note that in diskotic liquid crystals the size effects in this geometry are considerably larger than in ordinary three-dimensional crystals, since $(a/L')^{1/2} \gg a/L'$.

In three-dimensional crystals with anisotropy of the chain type, the size effects also have a different character. The point is that now we can already separate the one-dimensional mode connected with the synchronous compression of all the chains. This mode includes the displacement v of the atoms:

$$2W_t = \frac{Tx^2}{2\pi EL'^2}\int \frac{dt}{t^2} + \frac{Tx^2}{(2\pi)^3 E}\int \frac{dt\,d^2p}{t^2+\delta p^2}. \tag{24}$$

The justification for this subdivision is analogous to that presented above for Eq. (18). The three-dimensional integral is $\sim Tx^2/Ea$, and the one-dimensional, $\sim Tx^2L/EL'^2$. The size effects are noticeable at $L' < (La)^{1/2}$. Anisotropy of the chain only increases this inequality. Thus, in diskotic liquid crystals in the $\Lambda L' < L^2$ geometry the largest size effects take place at $x = 0$ and $q \neq 0$, whereas in three-dimensional chain crystals they appear more strongly at $x \neq 0$ and $q = 0$.

We proceed now to the diffuse scattering. Let q be close to the reciprocal-lattice vector, and let $x = 0$. In the harmonic approximation we then have from (12) for the contribution of the diffuse scattering to the structure factor

$$S_d(\mathbf{p}) = \int d^3R e^{i\mathbf{p}\mathbf{r}}\exp\{-\tau_i\tau_j[G_{ij}(\mathbf{R})-G_{ij}(\infty)]\}. \tag{25}$$

We have put here

$$\mathbf{p} = \mathbf{q} - \tau, \quad G_{ij}(\mathbf{R}) = \int \frac{d^3k}{(2\pi)^3}\langle u_i(\mathbf{k})u_j(-\mathbf{k})\rangle(1-\cos\mathbf{k}\mathbf{R}). \tag{26}$$

We begin with the calculation of the function $G_{ij} = G\delta_{ij}$. We consider again first the case $\Lambda L' \gg L^2$. We then have

$$G = \frac{T}{LC}\int \frac{d^2s}{(2\pi)^2}\frac{1}{s^2}(1-\cos s\mathbf{r}) + \frac{T}{C}\int \frac{d^2s\,dt}{(2\pi)^3}\frac{1}{s^2+\Lambda^2t^4}[1-\cos(s\mathbf{r}+tz)]. \tag{27}$$

Equation (27) has the same structure as (19). Again, the first term in (27) is connected with the contribution of the individual lattice layers, and the second with the three-dimensional fluctuations:

$$G = G_2 + G_3, \quad G_2 = \frac{T}{4\pi LC}\ln\frac{r}{a}, \tag{28}$$

$$G_3(\mathbf{R}) = I_1 + I_2(\mathbf{R}),$$

where

$$I_1 = \frac{T}{8\pi^2 C}\frac{1}{(a\Lambda)^{1/2}}\left\{\varphi\left(\frac{(a\Lambda)^{1/2}}{d}\right) - \varphi\left(\frac{(a\Lambda)^{1/2}}{L}\right)\right\}$$

[φ is the same function as in (19)];

$$I_2(\mathbf{R}) = -\frac{T}{4\pi^2 C}\int_{1/L}^{1/d} dt\,K_0(\Lambda t^2 r)\cos tz, \tag{29}$$

K_0 in (29) is a modified Bessel function of zeroth order. The integral that determines expression (29) can unfor-

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tunately be obtained only numerically. However, the asymptotic form of interest to us, at $z \ll (\Lambda r)^{1/2}$ but $z \gg d$, reduces to a calculation of the following known integral

$$\int_0^\infty \frac{du}{u} e^{-\Delta/u} \cos u, \quad \Delta = \frac{z}{(\Lambda r)^{1/2}}.$$

Thus, in this limiting case we have

$$I_3(\mathbf{R}) = -\frac{T}{8\pi C} \frac{1}{(\Lambda r)^{1/2}} \{K_0[(2\Delta)^{1/2}(1+i)]+K_0[(2\Delta)^{1/2}(1-i)]\}. \quad (30)$$

At $\Delta \ll 1$

$$I_3(\mathbf{R}) \approx \frac{T}{8\pi C} \frac{1}{(\Lambda r)^{1/2}} \ln \frac{z}{(\Lambda r)^{1/2}}. \quad (31)$$

Comparing expressions (28) for the "two-dimensional" contribution to the diffuse scattering and (31) for the "three-dimensional," we find that the size effects manifest themselves at $L^2 < L'$ for thicknesses L smaller than a certain critical value L_{d2}:

$$L_{d2} = \frac{8(\Lambda r)^{1/2}}{\ln(z^2/\Lambda r)} \ln(r/L'). \quad (32)$$

In the second limiting case $\Lambda L' < L^2$ we have in place of (27)

$$G(\mathbf{R}) = \frac{2\pi T}{CL'^2} \sum_{m,n} \int \frac{dt}{\Lambda^2 t^4 + (m^2+n^2)4\pi^2/L'^2}[1-\cos(tz+mx+ny)]. \quad (33)$$

After cumbersome transformation we obtain in the principal approximation in $1/L'$

$$G(\mathbf{R}) = \frac{T}{8\pi^{1/2}} \frac{1}{C} \frac{1}{(\Lambda r)^{1/2}} \left\{D_{-1/2}\left(\frac{\Delta}{2^{1/2}}\right)\right\}^2, \quad (34)$$

where $D_{-1/2}$ is a parabolic-cylinder function.

At $z \gg (\Lambda r)^{1/2}$ we have

$$G(\mathbf{R}) = \frac{T}{8\pi^{1/2}} \frac{1}{C} \frac{1}{z} \exp\left\{-\frac{z^2}{4\Lambda r}\right\}. \quad (35)$$

The size-effect corrections to the structure factor, just as for the case of coherent scattering, are of the order of $(a/L')^{1/2}$ and manifest themselves therefore at much larger thicknesses than in ordinary and anisotropic three-dimensional crystals with the appropriate type of anisotropy (chain structures).

The simplest to calculate is the structure factor of diffuse scattering under the condition that $p(a\Lambda)^{1/2} \ll 1$. The argument of the exponential in (25) is then small and we can replace the exponential by its argument. This means in fact that $S_d(\mathbf{p})$ is a linear combination of the correlators $\langle u_\alpha(\mathbf{p}) u_\beta(-\mathbf{p})\rangle$:

$$S_d(\mathbf{p}) = \exp(-2W_i) T \tau_\alpha \tau_\beta \langle u_\alpha(\mathbf{p}) u_\beta(-\mathbf{p})\rangle. \quad (36)$$

A contribution to the diffuse scattering is made also by the displacements v of the atoms in the liquid columns:

$$S_d \sim T/EL'^{1/2} \varkappa. \quad (37)$$

We shall not present the expressions for the diffuse-scattering structure factor, since they are very unwieldy, and describe the results only qualitatively. If the dimensions of the scattering region satisfy the condition $\Lambda L' \gg L^2$, we have two characteristic lengths, L_{c2} and L_{d2}. The value of L_{c2} is determined only by the parameters of the diskotic-liquid-crystal structure, by the temperature, by the elastic moduli, and by the dimensions. L_{d2} depends in addition on the considered scattering region, i.e., on the wave vectors p. From (32) and (20) it is easy to see that when the following inequalities are satisfied:

$$(\Lambda/p)^{1/2} \gg d, \quad \Lambda \varkappa^2/p \gtrsim 1$$

we always have

$$L_{d2} > L_{c2}.$$

We have thus in this case:

1) at $L < L_{c2} < L_{d2}$ the diffuse and coherent scatterings are determined by two-dimensional fluctuations. The structure factor is of the form[2,3]

$$S(\mathbf{p},0) \sim \Lambda^{-x} \frac{1}{n^{1-x}} + \delta(\mathbf{p}) L'^{(1-2x)}, \quad (38)$$

where the exponent $x = Tq^2/4\pi C$.

2) In the region $L_{c2} < L < L_{d2}$ the coherent scattering is already three-dimensional, but the diffuse scattering is still described by the first term of (38), i.e., it has a singular two-dimensional character.

3) Finally, at $L > L_{d2}$ both types of scattering are determined by the three-dimensional fluctuations.

In the $\Lambda L' < L_2$ geometry this division of the scattering into one-dimensional (chain) and three-dimensional contributions are impossible, for reasons already discussed. A one-dimensional contribution to the structure factor is obtained only for diffuse scattering and is due to the displacements v of the particles along the liquid columns. At $\varkappa \neq 0$ this contribution competes with the three-dimensional scattering by the displacements of the two-dimensional lattice of these columns.

Let us sum up. The structure factor of diskotic systems has a large number of peculiarities. It must be indicated first that, compared with three-dimensional systems, the role of diffuse scattering in diskotic liquid crystals is much greater. The point is that the Debye-Waller factor in diskotic liquid crystals is large, and the coherent scattering is therefore weaker. The ratio of the scattering intensities of both types in diskotic liquid crystals is larger than in ordinary three-dimensional ones, by a factor

$$\frac{C^{1/2} K^{1/2} \varphi((\Lambda a)^{1/2}/d)}{Ea^{1/2}\delta f(a\delta/d)} \sim 10^2,$$

where $f(u) = u \ln(1 + u^2) + 2\arctan u - 2u \ln u$, δ is the anisotropy parameter of the three-dimensional system, $C \sim 10^9$ erg/cm^3 is the elastic modulus of the diskotic liquid crystal, and $E \sim 10^{11}$ erg/cm^3 is the Young's modulus of the three-dimensional crystal.

The second difference of diskotic systems manifests itself in the presence of strong size effects at thicknesses when such effects no longer appear in the corresponding three-dimensional systems. Indeed, in an isotropic three-dimensional system the size effects manifest themselves at dimensions $R \sim a$. In an anisotropic system the size effects extend to large dimensions $L \sim d/\delta$ or $L' \sim a/\delta$. In diskotic liquid crystals the size effects are even stronger and extend to even larger thicknesses on account of the factor $\ln(L/(a\Lambda)^{1/2})$ or

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$\ln((L'\Lambda)^{1/2}/d)$.

We note also that the competition of the quasi-one-dimensional (or quasi-two-dimensional) fluctuations of the displacements in chain or layered structures can lead in principle to nonmonotonic size dependences of the structure factor. The point is that in the quasi-one-dimensional or the quasi-two-dimensional case the contribution to the coherent scattering cross section decreases with the size of the sample in the corresponding direction (owing to the divergence of the Debye-Waller factor), and the relative share of the diffuse background increases therefore. On going to the three-dimensional system, however, the usual size effects set in, wherein the coherent cross section becomes larger than the diffuse one.

In conclusion, the authors are sincerely grateful to I.E. Dzyaloshinskiĭ and S. Chandrasekhar for discussions and for interest in the work, as well as to V.L. Pokrovskiĭ, who pointed out an error in the initial treatment of the $\Lambda L' \ll L^2$ case.

[1)]This circumstance was pointed out to us by G. E. Volovik.

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Translated by J. G. Adashko